

## PATENT ABSTRACTS OF JAPAN

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### (54) LATEX FOR PAPER COATING

#### (57)Abstract:

**PURPOSE:** To provide a paper-coating latex containing two specific kinds of polymer latex containing butadiene component and giving a printing paper having high surface strength and stiffness and free from print nonuniformity.

**CONSTITUTION:** The objective latex is composed of (A) 65-95wt.% (in terms of solid) of a polymer latex composed of (i) 15-40wt.% of butadiene, (ii) 0.5-8wt.% of an ethylenically, unsaturated carboxylic acid and (iii) 52-84.5wt.% of copolymerizable other monomers, having an average particle diameter of 900-2,500 $\text{\AA}$ ; and giving a latex film having a glass transition temperature of -10 to +50°C and a get content of 60-95wt.% and (B) 5-35wt.% (in terms of solid) of a polymer latex composed of 50-80wt.% of the component (i), 0.5-8wt.% of the component (ii) and 12-49.5wt.% of the component (iii), having an average particle diameter of 900-2,500 $\text{\AA}$ ; and giving a latex film having a glass transition temperature of -30 to -70°C provided that the difference in the glass transition temperatures between the components A and B is  $\geq 30^\circ\text{C}$ .

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CLAIMS

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[Claim(s)]

[Claim 1]Latex for paper coating which consists of 65 to 95 % of the weight (solid content conversion) of the following polymer latex (A), and 5 to 35 % of the weight (solid content conversion) of polymer latex (B), and is characterized by a glass-transition-temperature difference of (A) and (B) being not less than 30 \*\*.

Polymer latex (A)

butadiene A 15-40 weight % ethylenic-unsaturated-carboxylic-acid monomer 0.5-8 weight % -- other copolymerizable monomers It consists of 52 to 84.5 % of the weight, and, Polymer latex (A) whose gel content glass transition temperature of a latex film obtained by having the mean particle diameter of 900-2500 A is -10-50 \*\*, and is 60 to 95%.

Polymer latex (B)

butadiene A 50-80 weight % ethylenic-unsaturated-carboxylic-acid monomer 0.5-8 weight % -- other copolymerizable monomers It consists of 12 to 49.5 % of the weight, and, Polymer latex (B) whose glass transition temperature of a latex film obtained by having the mean particle diameter of 900-2500 A is -30--70 \*\*.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to latex for paper coating. It is related with latex for paper coating for obtaining the print sheet which has good surface intensity and paper stiffness in sheet offset printing, and does not have printing unevenness especially in detail.

[0002]

[Description of the Prior Art]In order to give the printability and optical fitness of paper, on the stencil paper surface conventionally Kaolin, Inorganic pigments, such as calcium carbonate, titanium oxide, a satin white, and aluminium hydroxide, Coating of synthetic latex, such as styrene butadiene series latex, and the distemper which made the subject further water soluble polymers, such as starch, polyvinyl alcohol, and casein, as an auxiliary binder or water retention agents is carried out as a binder.

[0003]By the way, in sheet offset printing, the fall of the print job nature resulting from the shortage of paper stiffness has been posing a big problem especially recently with the weight saving of such coated paper, and improvement in the speed of print speed.

[0004]Although the correspondence from pulp combination of coating stencil paper, a degree of beating, and a loading material side can be considered as the measure, the actual condition is that examination does not progress easily in various restrictions. It is possible to improve the rigidity of a coating layer as another measure. the operable fall accompanying [ although it is increasing the amount of the starch used used as an auxiliary binder as an easy method ] the rise of paint viscosity, and quality of paper -- when the adverse effect to a field is taken into consideration, there is a fixed limit. Although it is also effective in paper stiffness grant to improve the rigidity of the latex polymer used as a binder, The actual condition is that the measures which produce big problems, like the fall of surface intensity serves as a coating layer which it is not avoided and the printing unevenness in an earth tone part tends to

generate, and can be satisfied enough are not established.

[0005]

[Problem(s) to be Solved by the Invention]In view of such a situation, this invention persons provide latex for paper coating for obtaining the print sheet which has good surface intensity and paper stiffness, and does not have printing unevenness.

[0006]

[Means for Solving the Problem]Namely, this invention consists of 65 to 95 % of the weight (solid content conversion) of the following polymer latex (A), and 5 to 35 % of the weight (solid content conversion) of polymer latex (B), And latex for paper coating, wherein a glass-transition-temperature difference of (A) and (B) is not less than 30 °C is provided.

Polymer latex (A)

butadiene 15-40 weight % ethylenic-unsaturated-carboxylic-acid monomer 0.5-8 weight % -- other copolymerizable monomers It consists of 52 to 84.5 % of the weight, and, Polymer latex (A) whose gel content glass transition temperature of a latex film obtained by having the mean particle diameter of 900-2500 Å is -10-50 °C, and is 60 to 95%.

Polymer latex (B)

butadiene 50-80 weight % ethylenic-unsaturated-carboxylic-acid monomer 0.5-8 weight % -- other copolymerizable monomers It consists of 12 to 49.5 % of the weight, and, Polymer latex (B) whose glass transition temperature of a latex film obtained by having the mean particle diameter of 900-2500 Å is -30-70 °C.

[0007]Hereafter, this invention is explained in detail. Butadiene used for polymer latex (A) is used in 15 to 40% of the weight of the range. If surface intensity sufficient at less than 15 % of the weight is not obtained and it exceeds 40 % of the weight, being revealed of paper stiffness becomes insufficient and it is not desirable. It is 20 to 35 % of the weight preferably.

[0008]Butadiene used for polymer latex (B) is used in 50 to 80% of the weight of the range. As for the improvement effect of printing unevenness, less than 50 % of the weight is insufficient, and if it exceeds 80 % of the weight, paper stiffness will fall, wet strength also falls further, and it is not desirable. It is 52 to 70 % of the weight preferably.

[0009]as an ethylenic-unsaturated-carboxylic-acid monomer used for the polymer latex (A) and (B), acrylic acid, methacrylic acid, itaconic acid, fumaric acid, maleic acid, etc. can be mentioned -- one sort -- or two or more sorts can be used. Polymer latex (A) and an ethylenic-unsaturated-carboxylic-acid monomer in (B) are used in 0.5 to 8% of the weight of the range, respectively. At less than 0.5 % of the weight, if mechanical stability and surface intensity fall and it exceeds 8 % of the weight, latex viscosity becomes high too much, it takes, treatment becomes difficult, and it is not desirable. It is 1 to 6 % of the weight preferably.

[0010]As other copolymerizable monomers used for the polymer latex (A) and (B), Styrene, alpha-methylstyrene, vinyltoluene, divinylbenzene, Which aromatic vinyl compound, methyl

acrylate, methyl methacrylate, Ethyl acrylate, ethyl methacrylate, butyl acrylate, 2-ethylhexyl acrylate, glycidyl methacrylate, dimethyl fumarate, Ethylenic-unsaturated-carboxylic-acid alkyl ester compounds, such as diethylfumarate, beta-hydroxyethyl acrylate, beta-hydroxyethyl methacrylate, Hydroxyalkyl group content compounds, such as hydroxypropyl acrylate and hydroxypropyl methacrylate, Amide system compounds, such as vinyl cyanide compounds, such as acrylonitrile and a methacrylonitrile, acrylamide, methacrylamide, and N-methylolacrylamide, are mentioned. Styrene, methyl methacrylate, acrylonitrile, beta-hydroxyethyl acrylate, and acrylamide are preferably used especially in these.

[0011]Other copolymerizable monomers in polymer latex (A) are used in 52 to 84.5% of the weight of the range. If being revealed of paper stiffness becomes insufficient [less than 52 % of the weight] and it exceeds 84.5 % of the weight, surface intensity falls and it is not desirable. It is 59 to 79 % of the weight preferably.

[0012]Other copolymerizable monomers in polymer latex (B) are used in 12 to 49.5% of the weight of the range. At less than 12 % of the weight, if paper stiffness and wet strength fall and it exceeds 49.5 % of the weight, the improvement effect of printing unevenness becomes insufficient and it is not desirable. It is 24 to 47 % of the weight preferably.

[0013]Glass transition temperature of polymer latex (A) needs to be in the range of -10-50 \*\*. - If paper stiffness falls at less than 10 \*\* and it exceeds 50 \*\*, surface intensity falls and it is not desirable. It is required to be in 60 to 95% of the weight of a range, if it separates from gel content of polymer latex (A) from this range, surface intensity falls and it is not preferred.

[0014]Glass transition temperature of polymer latex (B) needs to be in the range of -30--70 \*\*. - If wet strength falls at less than 70 \*\* and it exceeds -30 \*\*, improvement in printing unevenness cannot be expected and it is not desirable.

[0015]Each of polymer latex (A) and mean particle diameter of (B) needs to be in the range of 900-2500 Å. Since viscosity of latex becomes high too much in less than 900 Å, if handling becomes difficult and exceeds 2500 Å, surface intensity falls and it is not desirable. Preferably, it is 1000-2000 Å.

[0016]These polymer latex (A) and (B) is mixed so that it may become (A)65-95 % of the weight and (B)5-35 % of the weight by solid content conversion, respectively, and it is necessary to make it polymer latex (A) and a glass-transition-temperature difference of (B) be not less than 30 \*\* in this invention. If being revealed of a rate of polymer latex (A) of paper stiffness becomes insufficient [less than 65 % of the weight] and it exceeds 95 % of the weight, improvement in printing unevenness cannot be expected. Even if a glass-transition-temperature difference is less than 30 \*\*, improvement in printing unevenness cannot be expected, and the purpose of this invention is not attained.

[0017]As the above-mentioned polymer latex (A) and a manufacturing method of (B), publicly known emulsion polymerization methods, such as a continuation emulsion polymerization, a

package emulsion polymerization, a two-step emulsion polymerization, and a dividing addition emulsion polymerization, are employable, for example. On the occasion of an emulsion polymerization, an additive agent and an auxiliary agent which are used for general emulsion polymerizations, such as a publicly known emulsifier, a chain transfer agent, a polymerization initiator, and a chelating agent, can be used.

[0018]As an emulsifier, sulfuric ester salt of higher alcohol, alkylbenzene sulfonates, An alkyl diphenyl ether sulfonate, an aliphatic-sulfonic-acid salt, an aliphatic-carboxylic-acid salt, Nonionic surface-active agents, such as anionic surface-active agents, such as sulfuric ester salt of a nonionic surfactant, an alkyl ester type of a polyethylene glycol, an alkylphenyl ether type, and an alkyl ether type, are used by one sort or two sorts or more.

[0019]As a chain transfer agent, n-hexyl mercaptan, n-octyl mercaptan, t-octylmercaptan, n-dodecyl mercaptan, t-dodecyl mercaptan, Alkyl mercaptan, such as n-stearylmercaptan, dimethyl xantho gene disulfide, Xanthogen compounds, such as diethyl xantho gene disulfide and diisopropyl xantho gene disulfide, A alpha-methylstyrene dimer, TAPINOREN, tetramethylthiuramdisulfide, Thiuram system compounds, such as a tetraethylthiuram disulfide and tetramethylthiurammonosulfide, Phenol system compounds, such as 2,6-di-tert-butyl-4-methylphenol and styrene-ized phenol, Allyl compounds, such as allyl alcohol, dichloromethane, dibromomethane, halogenated hydrocarbon compounds, such as a carbon tetrachloride and carbon tetrabromide, triphenylethane, pentaphenylethane, an acrolein, a meta-acrolein, thioglycolic acid, 2-ethylhexyl thioglycolate, etc. are mentioned -- one sort -- or two or more sorts can be used.

[0020]As an initiator, an oil-soluble initiator or redox system initiators, such as water-soluble initiators, such as potassium persulfate, ammonium persulfate, and sodium persulfate, and benzoyl peroxide, can be used.

[0021]Latex for paper coating of this invention is adjusted as aqueous dispersion liquid with other auxiliary binders paints and also if needed.

[0022]Under the present circumstances, eight to 25 weight section and other auxiliary binders can carry out 0-30 weight-section use of the latex for paper coating of this invention to paints 100 weight section in solid content conversion. Since white paper gloss will become low and ink drying nature will worsen further if the amount of the latex for paper coating used of this invention runs short of surface intensity and exceeds 25 weight sections in less than eight weight sections, it is not desirable.

[0023]Here, as paints, inorganic pigments, such as kaolin clay, talc, barium sulfate, titanium oxide, calcium carbonate, aluminium hydroxide, a zinc oxide, and a satin white, and an organic color like polystyrene latex are mentioned, and these are used, independent or mixing.

[0024]As other auxiliary binders, synthetic latex, such as natural binders, such as denaturation starch, such as starch, an oxidized starch, and esterification starch, soybean protein, and

casein, polyvinyl alcohol, polyvinyl acetate latex, and acrylic latex, is used.

[0025]When adjusting distemper using latex for paper coating of this invention, further -- other auxiliary agents (sodium pyrophosphate and sodium polyacrylate.), for example, a dispersing agent defoaming agents (polyglycol and fatty acid ester.), such as hexametaphosphoric acid sodium leveling agents (turkey red oil.), such as phosphoric ester and silicone oil antiseptics, such as dicyandiamide and urea, and a water resistance-ized agent (formalin and a hexamine.) Release agents (calcium stearate, a paraffin emulsion, etc.), such as melamine resin, urea resin, and griot KISARU, fluorescent dye, and color water retention improvers (carboxymethyl cellulose, sodium alginate, etc.) are added if needed.

[0026]When adjusting distemper, after mixing the polymer latex (A) and (B) beforehand, it may blend with paints etc. and the polymer latex (A) and (B) may be independently added, respectively at the time of pigment dispersion.

[0027]Thus, an adjusted distemper constituent, A braid coating machine, an air knife coater which are used for general coat paper manufacture, an one machine or an off-machine coating machine which formed coating apparatus, such as a roll coater, a brush coating machine, a curtain coating machine, a bar coating machine, a photogravure coating machine, and a size press coating machine, -- a stencil paper top -- much more -- or coating is divided and carried out to a multilayer. Although solids concentration of a coating composition in that case is generally 40 to 70 % of the weight, it is more preferred than an operable field that it is 45 to 67% of the weight of a range.

[0028][Example] -- although an example is raised to below and this invention is concretely explained to it, this invention is not limited at all by these examples. The part and % which are used mean weight section and weight % altogether, as long as there is no notice.

[0029]- each compound of number of copies shown in the manufacture-10 l. resisting pressure container of polymer latex table-1, an emulsifier, and a chain transfer agent -- specified quantity preparation -- the emulsion polymerization was performed at 69 \*\*, preparing and agitating 0.8 copy of potassium persulfate, 0.4 copy of sodium bicarbonate, and 90 copies of pure water further. Each polymerization conversion of the obtained polymer latex was not less than 98%. Subsequently, after sodium hydroxide solution adjusted PH of polymer latex to 6.5, the unreacted monomer was removed in steam distillation and each polymer latex shown in table-1 was obtained.

[0030]It measures with a number-average-particle-diameter electron microscope. (Number average of the particle number 500)

[0031]A latex film is produced by gel content room temperature desiccation. About 1.0 g of latex films are correctly put into 400-cc toluene after weighing after that, the neglect dissolution is carried out for 48 hours, at a wire gauze of 300 meshes, after filtration, it dries, toluene insoluble (gel) on a wire gauze is measured, and gel content is computed.

[0032]A latex film was produced by glass-transition-temperature room temperature desiccation, and it measured using a differential scanning calorimeter.

[0033]

[Table 1]

ラテックスNo.	a-1	a-2	a-3	b-1	b-2	b-3	x-1	x-2	x-3	x-4
化合物-										
ブタジエン	20	35	30	55	65	70	30	25	45	90
スチレン	65	36	45	30	16.5	15	35	65	31	5
メチルメタクリレート	10	20	15	10	15	10	25	5	10	
アクリロニトリル		5	5				5			
β-ヒドロキシエチルアクリレート	2	1	2	2	1	2	1	2	1	2
イタコン酸	3		1	2				3		
アマル酸		1.5	2	1	2.5	2	2		2	
アクリル酸						1	2		1	
メタクリル酸		1.5								3
-連鎖移動剤-										
1-ドデシルメルカプタン	0.4	0.5	0.6	0.9	0.8	0.8	0.8	0.6	0.7	0.8
タービノレン		1.0				2.5	1.5	2.5		
α-メチルスチレンダイマー			1.0		2.0				1.0	2.5
-乳化剤-										
ドデシルベンゼンスルホン酸ソーダ	0.6	0.8	0.5	0.6	0.5	0.4	0.2	0.5	0.6	0.3
平均粒子径 (オングストローム)	1500	1150	1800	1250	1600	1820	2700	1650	1300	2300
ガラス転移温度 (℃)	30	5	15	-30	-50	-60	16	25	-10	-80
ゲル含有量 (%)	80	85	68	70	70	65	69	45	75	80

表-1



[0034]- Adjustment and quality assessment of a coating composition - A quality assessment as a binder for paper coating was carried out using each obtained polymer latex. As a paint formula was shown in table-2, coating conditions and surface-finish conditions are the passages of table-3.

[0035]

[Table 2]

塗料処方	
カオリンクレー	55部
炭酸カルシウム	45部
変性ゼンブン	3部
重合体ラテックス (合計)	12部

[0036]

[Table 3]

塗工および仕上げ条件	
原紙	坪量 55 g/㎡の上質紙
コーター	ブレードコーター
コート量	12 g/㎡ (片面)
塗工速度	100 m/m
乾燥	150℃×6秒 (熱風)
仕上げ条件	ベンチスケールスーパーカレンダー使用 50℃×55 Kg/cm×2 n i p s で処理

[0037]The following methods estimated the surface intensity of the obtained coated paper, paper stiffness, and printing unevenness. An evaluation result is shown in table-4 and table-5.

[0038]The grade of picking at the time of printing using dampening water with a wet strength RI printing machine was judged with the naked eye, and it evaluated in five steps of the 1st class

(the best) - the 5th class (the worst). 4 times of average value are shown.

[0039]The wet strength measuring method and the same method estimated except not using dry intensity dampening water.

[0040]Paper Two kinds of strip-of-paper-like coating specimens (15 mm in width) which become perpendicular with the direction of waist paper making and it were produced. Critical length was searched for with the Clerks stiffness tester with the conventional method, and the average value of the 2-way was computed, respectively. 4 times of average value are shown.

[0041]Using the printing unevenness RI printing machine, by the method of the trapping examination, 0.4 cc of 1 amorous-glance yellow ink and 2 amorous-glance red ink 0.3cc 2 color overprint was performed, and the transition homogeneity of the red ink of two amorous glance was evaluated by viewing. It judged in order of O - xx from what has few printing unevenness.

[0042]

[Table 4]

表-4

	実 施 例					比 較 例		
	1	2	3	4	5	1	2	3
-ラテックス配合- 重合体ラテックス (A) 重合体ラテックス (B) (A) / (B)	a-1 b-1 80/20	a-2 b-2 80/20	a-2 b-3 90/10	a-3 b-2 70/30	a-3 b-2 90/10	a-1 — 100/0	a-3 — 100/0	— b-1 0/100
	2.0	1.8	2.0	2.0	1.7	2.0	1.7	3.5
	2.0	1.5	1.5	1.8	1.6	2.5	1.5	2.5
-評価結果- ウェット強度 ドライ強度 紙 厚 (mm) 印刷ムラ	37	32	32	32	34	36	33	20
	○	◎	◎	◎	◎	xx	x	◎

[Table 5]

表-5

	比較例						
	4	5	6	7	8	9	10
ラテックス配合重合体ラテックス (A)	x-1	x-2	x-3	a-2	a-2	a-2	a-3
重合体ラテックス (B)	b-1	b-1	b-1	x-4	b-1	b-1	x-3
(A) / (B)	80/20	80/20	90/10	70/30	50/50	97/3	80/20
評価結果 - 評価結果 - ワエット強度	3.5	2.0	2.0	4.0	2.3	1.9	1.7
ドライ強度	2.2	3.8	1.8	2.5	1.8	2.2	1.4
紙 厚 (mm)	32	34	23	25	23	30	32
印刷ムラ	○	○	△	○	○	△	x

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EXAMPLE

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[Table 1]

表-1

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ー化合物ー										
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スチレン	65	36	45	30	16.5	15	35	65	31	5
メチルメタクリレート	10	20	15	10	15	10	25	5	10	
アクリロニトリル		5	5							
β-ヒドロキシエチルアクリレート	2	1	2	2	1	2	1	2	1	2
イタコン酸	3		1	2				3		
フマル酸		1.5			2.5	2			2	
アクリル酸			2	1		1	2		1	
メタクリル酸		1.5								3
ー連鎖移動剤ー										
トートデシルメルカプタン	0.4	0.5	0.6	0.9	0.8	0.8	0.6	0.6	0.7	0.8
タービノレン		1.0				2.5	1.5	2.5		
α-メチルスチレンダイマー			1.0		2.0				1.0	2.5
ー乳化剤ー										
ドデシルベンゼンスルホン酸ソーダ	0.6	0.8	0.5	0.6	0.5	0.4	0.2	0.5	0.6	0.3
平均粒子径 (オングストローム)	1500	1150	1800	1250	1600	1820	2700	1650	1300	2300
ガラス転移温度 (℃)	30	5	15	-30	-50	-60	16	25	-10	-80
ゲル含有量 (%)	80	85	68	70	70	65	69	45	75	80

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[0035]

[Table 2]

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変性デンプン	3部
重合体ラテックス (合計)	12部

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[Table 3]

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原紙	坪量 55 g/㎡の上質紙
コーター	ブレードコーター
コート量	12 g/㎡ (片面)
塗工速度	100 m/m
乾燥	150℃×6秒 (熱風)
仕上げ条件	ベンチスケールスーパーカレンダー使用 50℃×55 Kg/cm×2 n i p s で処理

[0037]The following methods estimated the surface intensity of the obtained coated paper, paper stiffness, and printing unevenness. An evaluation result is shown in table-4 and table-5.

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[0039]The wet strength measuring method and the same method estimated except not using dry intensity dampening water.

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become perpendicular with the direction of waist paper making and it were produced. Critical length was searched for with the Clerks stiffness tester with the conventional method, and the average value of the 2-way was computed, respectively. 4 times of average value are shown. [0041]Using the printing unevenness RI printing machine, by the method of the trapping examination, 0.4 cc of 1 amorous-glance yellow ink and 2 amorous-glance red ink 0.3cc 2 color overprint was performed, and the transition homogeneity of the red ink of two amorous glance was evaluated by viewing. It judged in order of O - xx from what has few printing unevenness.

[0042]

[Table 4]



表-4

	実 施 例					比 較 例		
	1	2	3	4	5	1	2	3
-ラテックス配合- 重合体ラテックス (A) 重合体ラテックス (B) (A) / (B)	a-1 b-1 80/20	a-2 b-2 80/20	a-2 b-3 90/10	a-3 b-2 70/30	a-3 b-2 90/10	a-1 — 100/0	a-3 — 100/0	— b-1 0/100
	2.0	1.8	2.0	2.0	1.7	2.0	1.7	3.5
	2.0	1.5	1.5	1.8	1.6	2.5	1.5	2.5
-評価結果- ウェット強度 ドライ強度 紙 厚 (mm) 印刷ムラ	37 ○	32 ◎	32 ◎	32 ◎	34 ◎	36 xx	33 x	20 ◎

[Table 5]

表-5

	比較例						
	4	5	6	7	8	9	10
ラテックス配合重合体ラテックス (A)	x-1	x-2	x-3	a-2	a-2	a-2	a-3
重合体ラテックス (B)	b-1	b-1	b-1	x-4	b-1	b-1	x-3
(A) / (B)	80/20	80/20	90/10	70/30	50/50	97/3	80/20
評価結果 - 評価結果 - ワエット強度	3.5	2.0	2.0	4.0	2.3	1.9	1.7
ドライ強度	2.2	3.8	1.8	2.5	1.8	2.2	1.4
紙 厚 (mm)	32	34	23	25	23	30	32
印刷ムラ	○	○	△	○	○	△	x

[Translation done.]